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Oxygenated derivatives of hydrocarbons

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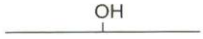
Arthropod waxes (complex mixtures of long-chain-carbon compounds) include straight-chain saturated and unsaturated hydrocarbons, methyl-branched hydrocarbons and more polar lipids that contain one or more oxygen functional groups on long aliphatic carbon chains that include wax esters, sterol esters, ketones, alcohols, aldehydes and acids for Insecta (Lockey, 1988; Buckner, 1993; Nelson and Blomquist, 1995) and Arachnida (Chapters 7 and 16, this book). As a major lipid class, hydrocarbons are present in the cuticular extracts of virtually all insects studied and there have been previous reviews on their occurrence, identification, biosynthesis and function (Jackson and Blomquist, 1976; Blomquist and Jackson, 1979; Blomquist and Dillwith, 1985; Blomquist *et al.*, 1987; Lockey, 1988; Blomquist *et al.*, 1993; Howard, 1993; Nelson and Blomquist, 1995; Howard and Blomquist, 2005). This chapter focuses on the occurrence, structural identification and function of those hydrocarbons that possess one or more oxygenated functional groups that include: ethers, epoxides, ketones, secondary alcohols, and their esters. These lipid classes represent hydrocarbon derivatives in which oxygen was biosynthetically introduced onto a non-terminal carbon(s) of long-chain hydrocarbons. Other lipid classes included in this review are long-chain methyl-branched primary alcohols and those wax esters with either ketone groups or methyl branches on their acid and/or alcohol moieties. This review does not include those oxygenated insect lipids not derived from pre-formed hydrocarbon constituents: long-chain fatty acids, primary alcohols, aldehydes, wax esters (esters of long-chain alcohols and long-chain acids), sterols, sterol esters, and mono-, di- and triacylglycerols.

Occurrence and structural identification

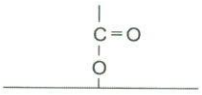
Secondary alcohols



Long-carbon-chain secondary alcohols (*sec*-alkanols) are not common constituents of insect cuticular lipids (Buckner, 1993). Espelie and Bernays (1989) reported that the cuticular lipids of *Manduca sexta* larvae reared on tomato or potato foliage contained

6–7% free C_{29} and C_{27} secondary alcohols. For tomato-reared larvae, the C_{29} carbon chain secondary alcohols were a mixture of positional isomers with the hydroxyl group at either C_8 (51%), C_9 (33%), C_{10} (10%), or C_7 (6%). The distribution for the C_{27} isomers was C_7 (52%), C_6 (28%), and C_8 (19%). The Dufour glandular secretion of *Myrmecocystus mexicanus* worker ants contained the three 2-alkanols, 2-tridecanol, 2-pentadecanol and 2-heptadecanol (Lloyd *et al.,* 1989). Approximately 2% of the cuticular lipids of the cabbage seedpod weevil, *Ceutorrhynchus assimilis*, are secondary alcohols with even and odd carbon-numbers ranging from 26 to 30 (Richter and Krain, 1980). The major components, secondary nonacosanol (95%) and hexacosanol (2%), were the same prominent secondary alcohols that are present in the host plant of this insect. The C_{21} secondary alcohol alkene enantiomers (6*Z*, 9*Z*, 11*S*)-6,9-heneicosadien-11-ol and (6*Z*, 9*Z*, 11*R*)-6-,9-heneicosadien-11-ol were identified as major sex pheromone components of female tussock moths, *Orgyia detrita* (Gries *et al.,* 2003) and the same C_{21} secondary alcohol di-alkene was identified as a major sex pheromone of the painted apple moth, *Teia anartoides* (El-Sayed *et al.,* 2005).

Secondary alcohol esters



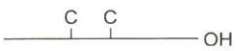
The occurrence of esters of secondary alcohols has been reported (Blomquist *et al.,* 1972; Warthen and Uebel, 1980; Pomonis *et al.,* 1993; Finidori-Logli *et al.,* 1996; Howard and Baker, 2003) and reviewed (Buckner, 1993; Nelson and Blomquist, 1995). Long-chain secondary alcohols are major constituents of the wax ester fraction from the cuticular lipids of six species of migratory grasshoppers, genus *Melanoplus*. These odd carbon-numbered C_{37}–C_{45} esters comprise 18 and 28% of the surface lipid of *M. sanguinipes* and *M. packardii*, respectively (Blomquist *et al.,* 1972). The secondary alcohol moieties of *M. sanguinipes* esters were C_{21} to C_{27} odd carbon-numbered compounds with the C_{23} compounds as major moieties (59%), and the major isomer as tricosan-11-ol, with smaller amounts of tricosan-10-ol. In the nymphs of *M. differentialis*, tricosanyl octadecanoate (C_{41}) and pentacosanyl hexadecanoate (C_{41}) are the major wax esters (Warthen and Uebel, 1980). The alcohol moieties are isomeric mixtures of 11- and 12-tricosanol and 8- and 9-pentacosanol. Adult *M. differentialis* have a different wax ester composition: tricosanyl octadecanoate (C_{41}) and pentacosanyl octadecanoate (C_{43}) with isomeric mixtures of 10-, 11- and 12-tricosanol and 11- and 12-pentacosanol respectively, as the secondary alcohol moieties (Warthen and Uebel, 1980). Odd-chain wax esters (C_{31}–C_{41}) with secondary alcohols as alcohol moieties are major components (18–30%) of the cuticular lipids of the migratory grasshoppers, *M. bivittatus, M. femurrubrum* and *M. dawsoni* (Jackson, 1981). Six unbranched and seven methyl-branched acetate ester homologs of long-chain (C_{29}) secondary alcohols (3-hydroxy to 8-hydroxy) were identified in the cuticular lipids of the

female screwworm fly, *Cochliomyia hominivorax* (Pomonis *et al.*, 1993). The cuticular lipids of the adult male little housefly, *Fannia canicularis*, contained 27% of the acetate ester of the secondary alcohol, 8-heneicosanol (Uebel *et al.*, 1977). The secondary alcohol acetate ester, 2*S*,12*Z*-2-acetoxy-12-heptadecene, was identified as the major sex pheromone component of the pistachio twig borer, *Kermania pistaciella* (Gries *et al.*, 2006). Small quantities of novel esters of long-chain secondary alcohols (C_{25}–C_{32}) and short-chain acids (C_2–C_4) were reported in hexane extracts of the male antenna and forelegs of *Helicoverpa zea* and *Heliothis virescens* (Böröczky *et al.*, 2008). The C_{25} and C_{27} secondary alcohol moieties for both species were identified as 7- and 8-pentacosanol and 8- and 9-heptacosanol respectively.

Diols

Diols have been rarely observed in insect cuticular lipids (Buckner, 1993). Odd-carbon-number diols (C_{23}–C_{29}) were the major lipid class (55%) of the larval cuticular lipids from the flour beetle, *Tenebrio molitor* (Bursell and Clements, 1967). The major diol constituent was 8, 9-pentacosanediol. For the cuticular lipids of *M. sexta* larvae, very small amounts (<1%) of 7,8- and 8,9-C_{27} diols and 8,9- and 9,10-C_{29} diols were identified (Espelie and Bernays, 1989). Hydroxy *n*-alkanols are diols with a hydroxyl functional group on the C_1 position (terminal) of the alkyl chain, but are technically not alcohol derivatives of hydrocarbons. There are a few reports of the occurrence of insect hydroxy *n*-alkanols (Buckner, 1993; Nelson and Blomquist, 1995; Buckner *et al.*, 1996). In a structure analysis study of beeswax, the major alcohol moieties of the diester fraction were identified as 1,23-tetracosanediol (42.2%), 1,27-octacosanediol (26.0%) and 1,25-hexacosanediol (20.2%) (Tulloch, 1971). The hydroxy *n*-alkanols comprised 16% of the cuticular lipids of *H. zea* pupae and were identified as C_{30}–C_{36} even-chain *n*-alcohols with hydroxyl groups on carbon numbers 11, 12, 13, 14, or 15 (Buckner *et al.*, 1996). Mass spectral analysis indicated the presence of unsaturation in the alkyl chain of the major diol components.

Methyl-branched alcohols



Very-long-chain methyl-branched alcohols (C_{38} to $>C_{44}$) and their esters with short-chain acids (C_2 to C_5) represent a novel class of long-chain internal lipids which mainly occur during insect metamorphosis (Nelson, 1993). The very-long-chain methyl-branched alcohols were first characterized in the internal lipids of developing pupae (pharate adults)

of the cabbage looper, *Trichoplusia ni* (Nelson *et al.,* 1989). The major alcohols had carbon backbones of 38, 40 and 42 carbons with 1, 2 or 3 methyl branches and occurred in 4 homologous series. The major alcohol components of each of the series respectively, were 24-methyltetracontan-1-ol, 24,28-dimethyltetracontan-1-ol, 24,36-dimethyltetracontan-1-ol, and 24,28,36-trimethyltetracontan-1-ol. These constituents existed in the internal lipids of the pupa both as free alcohols and as ester components. The acid moiety of the very-long-chain methyl-branched alcohol esters was identified as acetic acid (Nelson and Blomquist, 1990). Neither the free alcohols nor their esters were found in the surface lipid of any stage of the cabbage looper.

The internal lipids of developing pupae of *M. sexta* contained long-chain methyl-branched alcohols (C_{25} to C_{32}) (Nelson *et al.,* 1990). These alcohols occurred as mixtures of monomethyl- and dimethyl-branched isomers in which the methyl branches were closer to the hydroxyl end of the molecule than to the alkyl end of the molecule, the opposite of that observed for the very-long-chain methyl-branched alcohols (C_{38} to $>C_{44}$) (Nelson and Fatland, 1992). The long-chain methyl-branched alcohols occurred mainly as acetate esters (Nelson *et al.,* 1990) with minor amounts of propionate esters (Nelson and Fatland, 1992). The propionate esters have only been characterized in *M. sexta*. In addition to their presence in developing pupae, small amounts of the alcohols and their acetate esters were identified in the internal lipids of larvae and adults of *M. sexta*. The very-long-chain methyl-branched alcohols (C_{35} to $>C_{46}$) and their acetate esters have also been identified in the internal lipids of pupae of the southwestern corn borer, *Diatraea grandiosella* (Nelson and Blomquist, 1990; Nelson and Fatland, 1997), the southern armyworm, *Spodoptera eridania* (Guo *et al.,* 1992), and in the tobacco budworm, *H. virescens*, the corn earworm, *H. zea*, the sunflower moth, *Homoeosoma electellum* and the banded sunflower moth, *Cochylis hospes* (Nelson and Fatland, 1997). Minor amounts of long-chain methyl-branched alcohols (C_{25}–C_{34}) were also found mainly in *H. virescens* and *H. zea* (Nelson and Fatland, 1997).

Ethers

Aliphatic ethers have been observed in cuticular lipids from a few insect species. The surface lipids of the locust, *L. m. cinerascens* contained 4–5% aliphatic ethers (Génin *et al.,* 1987). The major ethers were C_{29}, C_{31} and C_{33} compounds with the alkyl moieties ranging in size from 11 to 20 carbons. The locust showed dimorphism: solitary locusts had a majority of the longer-carbon-chain ethers while the gregarious locusts had a majority of shorter-carbon-chain ethers. The surface lipids of the red-shouldered leaf beetle, *Monolepta australis*, contained a series of 7-octadecenyl alkyl ethers, the major constituent being 7-octadecenyl pentadecyl ether (Southwell and Stiff, 1989).

Epoxides

Epoxy derivatives of n-alkanes

The occurrence of hydrocarbons (usually mono- and di-alkenes) with an epoxide function group have been reported usually as sex attractants. The sex attractant of the female gypsy moth, *Lymantria dispar*, was identified as the C_{18} 2-methyl alkane derivative *cis*-7,8-epoxy-2-methyloctadecane (Bierl *et al.,* 1972). For the housefly, *M. domestica*, a major sex pheromone component is the C_{23} *n*-alkane epoxide *cis*-9,10-epoxytricosane (Uebel *et al.,* 1978) with a lesser quantity of 9,10-epoxyheptacosane (Mpuru *et al.*, 2001).

Epoxy derivatives of mono-alkenes

C_{19} mono-alkenes with an epoxide functional group include the lepidopteran female sex pheromones 9-*cis*-(*Z*)-6,7-epoxy-nonadecene and 6-*cis*-(*Z*)-9,10-epoxy-nonadecene of the geometrid moths, *Biston robustum* (Yamamoto *et al.,* 2000) and the common forest looper, *Pseudocoremia suavis* (Gibb *et al.,* 2006), respectively. The first epoxide of a C_{21} mono-alkene, (6Z)-*cis*-9,10-epoxyheneicosene, was first described by Rollin and Pougny (1986) as a pheromone component of the ruby tiger moth, *Phragmatobia fuliginosa*. A novel C_{21} di-epoxide pheromone component, 3*Z*-*cis*-6,7-*cis*-9,10-diepoxyheneicosene was first identified from the lepidopteran, *Leucoma salicis* (Gries *et al.,* 1997) and more recently, (3*R*,4*S*,6*S*,7*R*, 9*Z*)-3,4–6,7-diepoxyheneicosene was identified in the pheromone gland of the clear-winged tussock moth, *Perina nuda* (Wakamura *et al.,* 2002).

Epoxy derivatives of di-alkenes

For C_{19} epoxy di-alkenes, identified sex attractants for geometrid moths include 3*Z*,9*Z*-6-,7-epoxy-nonadecadiene, *Eufidonia convergaria* (Millar *et al.,* 1990a) and *B. robustum* (Yamamoto *et al.,* 2000); 6*Z*,9*Z*-3,4-epoxy-nonadecadiene, *Probole amicaria* (Millar *et al.,* 1990b) and *Milionia basalis pryeri* (Yasui *et al.,* 2005); and 3*Z*,6*Z*-9,10-epoxy-nonadecadiene, *P. suavis* (Gibb *et al.,* 2006). For the noctuid moth, *Rivula propinqualis*, 3*Z*,9*Z*-6,7-epoxy-nonadecadiene was identified in the female pheromone-gland extract (Millar *et al.,* 1990a). Components of the tiger moth (*Arctia caja*) sex pheromone were identified as the C_{20} and C_{21} epoxides, (3*Z*, 6*Z*)-*cis*-9,10-epoxyeicosadiene and 3*Z*,6*Z*-*cis*-9,10-epoxyheneicosadiene (Bestmann *et al.,* 1992). The same 9,10-epoxy C_{21} di-alkene was a sex pheromone component of the saltmarsh caterpillar moth, *Estigmene acrea* (Hill and Roelofs, 1981) and ruby tiger moth, *P. fuliginosa* (Rollin and Pougny, 1986). The pheromone glands of the geometrid moth species, *Semiothisa signaria dispuncta*, *Caenurgina distincta* and *Euclidea cuspidea,* produced pheromone blends that contained the C_{17}, C_{20} and C_{21} epoxy alkenes, 6*Z*,9*Z*-cis-3,4-epoxyheptadecadiene (Millar *et al.,* 1987), 3*Z*,6*Z*-*cis*-9,10-epoxyeicosadiene and 3*Z*,6*Z*-cis-9,10-epoxyheneicosadiene, respectively (Millar *et al.,* 1991).

Ketones

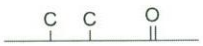
Ketones as cuticular lipids

Like secondary alcohols, ketones are not common constituents of the cuticular lipids of insects (Lockey, 1988). The cuticular lipid of the female housefly, *M. domestica*, contains 6% of an unsaturated ketone, (*Z*)-14-tricosen-10-one (Uebel *et al.,* 1978) and lesser amounts of tricosan-10-one and heptacosen-12-one (Mpuru *et al.,* 2001). The cuticular lipids of several species of *Drosophila* contain C_{13}–C_{17} saturated and unsaturated ketones, including 2-tridecanone and 2-pentadecanone in *Drosophila hydei* (Moats *et al.,* 1987), 10-heptadecen-2-one in *D. mulleri* (Bartelt *et al.,* 1989), and 2-pentadecanone in *D. busckii* (Schaner *et al.,* 1989). Odd-chain ketones (2-nonadecanone, 2-heneicosanone and 2-tricosanone) comprise 1% and 3% of adult male and female cuticular lipids, respectively, of the pecan weevil, *Curculio caryae* (Espelie and Payne, 1991). The cuticular lipids of mature screwworm females, *C. hominivorax*, contained small quantities of two C_{31} ketones: the symmetrical ketone, 16-hentriacontanone and the methyl-branched ketone, 21-methyl-7-hentriacontanone (Pomonis *et al.,* 1993).

Ketones as glandular lipids

Long-chain ketones have been reported as semiochemicals in lipid mixtures of specialized glands. (*Z*)-10-Heptadecen-2-one was identified in surface lipids and the ejaculatory bulb of *D. martensis, D. buzzatii* and *D. serido* (Schaner and Jackson, 1992). Both (*Z*)-10-heptadecen-2-one and 2-tridecanone were synthesized by the microsomal fraction of the ejaculatory bulbs from mature male *D. buzzatii* (Skiba and Jackson, 1993). Identified ketohydrocarbons from moth pheromone gland components include: the C_{21} keto monoenes, (*Z*)-6-heneicosen-11-one of the Douglas-fir tussock moth, *Orgyia pseudotsugata* (Smith *et al.,* 1975) and (Z)-6-heneicosen-9-one, *O. thyellina* (Gries *et al.,* 1999); the C_{21} keto di-alkene, (*Z,E*)-6,8-heneicosadien-11-one of the Douglas-fir tussock moth, *O. pseudotsugata* (Gries *et al.,* 1997) and the western tussock moth *O. vetusta* (Gries *et al.,* 2005). Lipids from Dufour gland secretions of ants in the genus *Myrmecocystus* included a homologous series of the odd-chain ketones 2-tridecanone, 2-pentadecanone and 2-heptadecanone (Lloyd *et al.,* 1989). Two keto mono-alkenes, 10-nonacosen-2-one and 16-pentacosen-2-one, were identified in the postpharyngeal gland lipids of the male solitary European beewolf wasp, *Philanthus triangulum* (Schmidt *et al.,* 1990; Herzner *et al.,* 2007a). The lipids of the postpharyngeal gland secretion of female *P. triangulum* that is used to embalm paralyzed prey include the two keto mono-alkenes Δ-16-pentacosen-8-one and Δ-18-heptacosen-8-one (Herzner *et al.*, 2007b).

Methyl-branched ketones



The major cuticular lipids of the German cockroach, *Blattella germanica,* have been identified as homologous series of straight chain and methyl-branched C_{27} and C_{29} alkanes (Augustynowicz *et al.,* 1987; Jurenka *et al.,* 1989). The cuticular lipids of *B. germanica* also contained long-chain ketones that were characterized as contact (nonvolatile) sex pheromones (Nishida and Fukami, 1983; Jurenka *et al.,* 1989). The major component is the dimethyl ketone 3,11-dimethylnonacosan-2-one, with lesser amounts of 29-hydroxy-3,11-dimethylnonacosan-2-one, 29-oxo-3,11-dimethylnonacosan-2-one and the C27 isomer, 3,11-dimethylheptacosan-2-one (Nishida and Fukami, 1983; Jurenka *et al.,* 1989). Recently, two other oxygenated derivatives of the C_{27} dimethyl-branched alkanes, 27-oxo-3,11-dimethylheptacosan-2-one and 27-hydroxy-3,11-dimethylheptacosan-2-one, were identified as components of the German cockroach contact pheromone (Eliyahu *et al.,* 2008).

Keto-alcohols, keto-aldehydes and keto-wax esters

In addition to the occurrence of the ketone functional group on *n*-alkanes and methyl-branched alkanes of insect lipids, they have been reported as functional groups on long-chain aldehydes, *n*-alcohols and acids (Buckner, 1993). For the lepidopteran pupae of *M. sexta* and *H. zea*, the major pupal cuticular lipids were identified as long-chain oxoaldehydes and oxoalcohols (Buckner *et al.,* 1984b; Buckner *et al.,* 1996) and for *M. sexta*, short-chain acid esters of oxoalcohols (Buckner *et al.,* 1984a). Surface lipid of diapausing *M. sexta* pupae consisted mainly of 11- and 12-oxooctacosanol, most of which (35–45%) was esterified to 3-oxobutyric acid (Buckner *et al.,* 1984a), and long-chain oxoaldehydes (30–35%) with the major constituents as 11- and 12-oxooctacosanal (Buckner *et al.,* 1984b). Oxoalcohols (mainly 12-oxotriacontanol) and oxoaldehydes (mainly 12-oxotriacontanal) were reported as minor components of the cuticular lipid of *H. zea* (Buckner *et al.,* 1996). Novel wax esters containing ketone groups on both very-long-chain acid and alcohol moieties have been identified in several homopteran insects. The surface wax of the cochineal insect, *Coccus cacti* and the woolly alder aphid, *Prociphilus tessellatus*, contain mainly the C_{66} ester, 15-oxotetratriacontanyl 13-oxodotriacontanoate (Chibnall *et al.,* 1934; Meinwald *et al.,* 1975). The cuticular lipid of the white pine chermes aphid, *Adelges (Pineus) strobi* includes a C_{66} wax ester composed of 17-oxohexatriacontan-1-ol and 11-oxotriacontanoic acid (Blount *et al.,* 1937). The major oxoalcohol and oxoacid moieties of the diketo

esters of the woolly apple aphid, *Eriosoma lanigerum*, are 15-oxotetratriacontan-1-ol and 13-oxodotriacontanoic acid (Cameron and Drake, 1976). The C_{64} ester, 15-oxo-tetratriacontanyl 11-oxo-triacontanoate, is the main constituent in the wax of the cochineal insect, *Dactylopius confusus* (Meinwald *et al.,* 1975), the lantern bug, *Cerogenes auricoma* and the related fulgorid species, *Fulgora castresii* (Mason *et al.,* 1989). The wax of another fulgorid species, *F. lampetis*, has 17-oxo-hexatriacontanyl 11-oxo-triacontanoate (C_{66}) as the major keto wax ester, but it also contains minor amounts of C_{44}–C_{54} normal carbon chain wax esters (Mason *et al.,* 1989).

Function of oxygenated hydrocarbons

The cuticular or surface lipids of arthropods are necessary for survival and among the many insect species cuticular lipids play a major role in minimizing water loss, in chemical communication, and in providing a wide range of other functions (Hadley, 1981; Blomquist and Dillwith, 1985; Noble-Nesbitt, 1991; St. Leger, 1991; Buckner, 1993; Nelson and Blomquist, 1995; Howard and Blomquist, 2005; see relevant subject chapters, this book). The functions of oxygenated derivatives of hydrocarbons have mainly been studied and reported in regard to their effects on protecting insects against desiccation and their role(s) in insect chemical communication.

Protective water barrier

The main function of cuticular lipid on terrestrial arthropods is to minimize the loss of water by transpiration across the integument; the lipids provide a better waterproofing barrier when they are in a solid rather than fluid state (Gibbs, 1998; Rourke and Gibbs, 1999; Rourke, 2000; Gibbs, 2002; Gibbs and Rajpuhorit, Chapter 6, this book). The introduction of a functional group (i.e., ester linkage, methyl branch, double bond, ketone, secondary alcohol) to the long, hydrophobic alkyl chain can introduce a kink in the lipid chain and disrupt lipid packing. A kink can result in increased fluidity and decrease in the melting temperature. Methyl branching gives lipid increased fluidity over a range of temperatures, and unsaturated hydrocarbons melt at a much lower temperature than their corresponding *n*-alkanes (Lockey, 1988; Gibbs and Pomonis, 1995). The presence of an ester linkage in long-chain wax esters has been shown to substantially lower the melting temperature relative to hydrocarbons containing the same number of carbon atoms (Gibbs and Pomonis, 1995; Patel *et al.,* 2001). Wax esters may interact with hydrocarbons to affect the properties of the overall lipid mixture (Riederer and Schneider, 1990; Gibbs, 1995; Dodd and Afzal-Rafii, 2000). Experimental data on the interactions between wax esters and *n*-alkanes showed a slight reduction in lipid melting temperature ($\leq 5°$ C) (Patel *et al.,* 2001).

In addition to wax esters, the inclusion of a mid-chain keto or alcohol functional group to a long-chain hydrocarbon would cause a kink in the lipid chain and result in cuticular lipids with lower melting temperatures. An example is provided by the wax esters of secondary

alcohols, which occur on melanopline grasshoppers (Blomquist *et al.,* 1972; see above, this chapter). Structurally, these esters of secondary alcohols are T-shaped molecules that pack less closely than esters of primary alcohols, and Patel *et al.* (2001) showed that the secondary wax esters of grasshoppers (*M. sanguinipes*) melted >60°C below primary esters of the same molecular weight. The quantity of lipid on the cuticular surfaces of diapausing pupae of the tobacco hornworm, *M. sexta* was three times that of non-diapausing pupae (Bell *et al.,* 1975) and those lipids include large amounts of oxoaldehydes and oxoalcohols esterified to 3-oxobutyric and 3-hydroxybutyric acids (Buckner *et al.,* 1984a, b). The presence of mid-chain ketone groups could act to increase the fluidity of the mixture of highly oxygenated cuticular lipids during deposition.

For the long- and very-long-methyl-branched alcohols and their esters that occur internally in the mid-pupal stages of Lepidoptera (Nelson, 1993; see above, this chapter), the fate and function of these alcohols have not been established. They are not synthesized and are at low levels or undetectable in larvae and adults, and at the beginning and end of the pupal stage (Dwyer *et al.,* 1986; de Renobales *et al.,* 1989; Nelson *et al.,* 1990; Guo *et al.,* 1992; Nelson, 1993). Nelson and Fatland (1997) suggest that their presence in mid-stage pupae suggests a role in metamorphosis, but further research would be required to establish a definitive physiological role for the methyl-branched alcohols and their acetate esters in lepidopteran pupae.

Chemical communication

The majority of the known cuticular lipid constituents that function in chemical communication processes are hydrocarbons (Howard and Blomquist, 1982; Blomquist and Dillwith, 1985; Howard, 1993; Nelson and Blomquist, 1995). Most oxygenated lipids that function as pheromones are not part of the surface lipids but are secretory products of specialized glands (Tamaki, 1985; Arn *et al.,* 1986; Morgan and Mandava, 1988). Many of the compounds in pheromones are short-chain unsaturated aldehydes, ketones and acetate esters of short-chain (C_{10}–C_{14}) unsaturated alcohols. Those short-chain lipids ($<C_{16}$) with biological activity have been reviewed elsewhere (Blomquist and Dillwith, 1985; Tamaki, 1985; Lockey, 1988; Blomquist *et al.,* 1993; Jurenka and Roelofs, 1993; Howard, 1993).

Ketones and secondary alcohols

An unsaturated ketone (*Z*)-14-tricosen-10-one, a prominent (6%) constituent of the cuticular lipid of the female housefly, *M. domestica*, is the major component of the sex pheromone mixture (Uebel *et al.,* 1978). For several species of *Drosophila*, the cuticular lipids contain saturated and unsaturated ketones (C_{13}–C_{17}) which were characterized as components of aggregation pheromones. Identified structures included 2-tridecanone and 2-pentadecanone in *D. hydei* (Moats *et al.,* 1987), (*Z*)-10-heptadecen-2-one in *D. mulleri* (Bartelt *et al.,* 1989), and 2-pentadecanone in *D. busckii* (Schaner *et al.,* 1989). The ejaculatory bulb and surface lipids of three *Drosophila* species (*D. martensis, D. buzzatii* and *D. serido*) had the compound (*Z*)-10-heptadecen-2-one that functions as the major

component of the aggregation pheromone of those insects (Schaner and Jackson, 1992). Both (*Z*)-10-heptadecen-2-one and 2-tridecanone (an inhibitor of aggregation) were synthesized by the microsomal fraction of the ejaculatory bulbs from mature male *D. buzzatii* (Skiba and Jackson, 1993). The C_{19} keto alkenes 10-nonacosen-2-one and 16-pentacosen-2-one, from the postpharyngeal gland of the male solitary wasp, european beewolf (*P. triangulum*), were identified as marking pheromones to attract females (Schmidt *et al.,* 1990; Kroiss *et al.*, 2006; Herzner *et al.,* 2007a).

Two acetate esters of mono-methyl-branched secondary alcohols were identified as major components of the contact mating pheromone of the New World screwworm *C. hominivorax*. Five homologous acetate derivatives of long-chain secondary alcohols and a related ketone, as identified by Pomonis *et al.* (1993) (see above in this chapter), were chemically synthesized (Furukawa *et al.,* 2002) and the two acetate esters of C_{29} secondary alcohols racemic 6-acetoxy-19-methylnonacosane and 7-acetoxy-15-methylnonacosane were characterized as sex stimulant pheromones (Carlson *et al.,* 2007). These two acetate derivatives were the first sex pheromones identified in a calliphorid fly. In the hymenopteran parasitoid *Diglyphus isaea*, long-chain secondary alcohol esters present on the females had an aphrodisiac effect on males. The major components were C_{21}–C_{25} 11-hydroxy esters of C_8 and C_{10} fatty acids (Finidori-Logli *et al.*, 1996). Secondary alcohols as pheromone components were reported for the first time in a ditrysian lepidopteran species. (6*Z*,9*Z*,11*S*)-6,9-Heneicosadiene-11-ol and (6*Z*,9*Z*,11*R*)-6,9-heneicosadiene-11-ol were identified as the major sex pheromone components of female tussock moths, *O. detrita* (Gries *et al.,* 2003). These two C_{21} *sec*-alcohol di-alkenes, in combination but not singly, attracted significant numbers of male moths.

Methyl-branched ketones (German cockroach pheromone)

As discussed earlier in this chapter, the occurrence of dimethyl-branched ketone components of the surface lipids of the German cockroach, *B. germanica*, has been reported and shown to have contact sex pheromone activity (Nishida and Fukami, 1983; Jurenka *et al.,* 1989; Blomquist, Chapter 3, this book). Structurally, the mixture of pheromone components all have methyl-branched positions at carbons 3 and 11 and the keto functional group at the carbon 2 position. Biosynthetic studies demonstrated that the methyl ketone pheromone component is produced by a sex-specific hydroxylation of 3,11-dimethylnonacosane to the corresponding 3,11-dimethylnonacosan-2-ol (by females only), which is then oxidized to the di-methyl ketone (by both females and males) (Chase *et al.,* 1992; Blomquist, Chapter 3, this book). Recently, two additional C_{27} components of the contact pheromone mixture of the German cockroach were identified: 27-oxo-3,11-dimethylheptacosan-2-one and 27-hydroxy-3,11-dimethylheptacosan-2-one (Eliyahu *et al.,* 2008). Even though it is not a hydrocarbon derivative, a volatile female sex pheromone that attracts *B. germanica* males over some distance was discovered (Liang and Schal, 1993) and has been identified as gentisyl quinone isovalerate, a short alkyl chain ester of an alcohol derivative (gentisyl quinone) of *p*-benzoquinone (Nojima *et al.,* 2005).

Epoxides

Most epoxides that have been characterized are epoxy derivatives of *n*-alkanes, mono-alkenes and di-alkenes that function as pheromone and sex attractant components, and the occurrence of many of them is reviewed above in this chapter. Epoxides are usually biosynthetically derived from monoene and polyene long-chain hydrocarbons and many are used as pheromone components and sex attractants by four macrolepidopteran families: the Geometridae, Noctuidae, Arctiidae, and Lymantriidae (Millar, 2000; Millar, Chapter 18, this book). As of 2009, sex pheromones or attractants have been identified for more than 120 geometrids (El-Sayed, 2009).

Pheromone databases

Recently, comprehensive World Wide Web (Internet) databases have been established on insect pheromones and semiochemicals: "The Pherolist", a database of chemicals identified from sex pheromone glands of female lepidopteran insects and other chemicals attractive to male moths (Arn *et al.*, 1999); and "The Pherobase", a database of pheromones and semiochemicals for Lepidoptera and other insect orders (El-Sayed, 2006). These large databases on behavior modifying chemicals have extensive cross-linkages for animal taxa, indexes of compounds and source (reference) indexes. The indexes include those compounds cited in this chapter and many more with pheromone and semiochemical function: acetate esters, diols, epoxides, ethers, ketones and secondary alcohols. For example, "The Pherolist" reports approximately 90 epoxy derivatives of C_{17}–C_{23} of *n*-alkanes, mono-alkenes and di-alkenes as insect semiochemicals.

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